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Optimization of hardness removal using response surface methodology from wastewater containing high boron by Bigadiç clinoptilolite

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ABSTRACT

In this study, hardness removal from wastewater containing a high concentration of boron by raw and modified clinoptilolite minerals was investigated. The raw clinoptilolite mineral was modified with HCl and NaOH. Optimum conditions for total and calcium hardness removal from the wastewater were determined by central composite design (CCD) of response surface methodology (RSM). The clinoptilolite dosage, contact time, temperature and dilution ratio were selected as independent variables. Equations that give removal efficiency (%) and removal capacity (mg/g) of total and calcium hardness were obtained through RSM analysis and interactions of independent variables with each other were illustrated by contour graphs. All determination coefficients (R^2) were above 0.90. The highest values of removal efficiency (%) and capacity (mg/g) were obtained by NaOH-modified clinoptilolite and its maximum values were above 99% and 12.30 mg/g, respectively.

Keywords: Hardness; Boron; Clinoptilolite; Response surface methodology (RSM)

1. Introduction

The hardness in the water is due to the polyvalent metal cations [1]. The ions of calcium, magnesium, iron, strontium, manganese and other some metal cause the hardness increase in water. The most effective ions that form hardness in water are calcium and magnesium [2]. The hardness of drinking water does not cause significant problems in terms of health, but it causes stratification in household appliances and increases the consumption of detergent and soap. In the industrial processes, the calcium cation reacts with carbonate or bicarbonate ions to form calcium carbonate precipitation. The calcium carbonate accumulated in the inner walls of pipes, steam boilers, and heat exchangers narrows the hydraulic passageway and reduces heat transfer efficiency. The carbonate formation leads to energy loss because of the increasing pressure drop in fluid systems [3]. There are various methods for softening of hard water such as chemical precipitation, adsorption, ion exchange, extraction and membrane processes [4].

Boron compounds have many uses in industry and boron is a critical parameter using environmental pollution. Boron has a toxic effect on plants, animals, and humans when above limit values in water. In that case, it must be treated before discharged to the environment [5–10]. There are various processes for boron removal from wastewater such as membrane distillation [11], adsorption [12], ion exchange [13], reverse osmosis (RO) [14,15], electrocoagulation [16] and etc. In case the membrane processes ended with RO are selected as a boron treatment method, the high amount of hardness in the wastewater causes the stratification and clogging on membrane surfaces [14]. The stratification causes a serious technical problem and a big economic burden for different industrial applications [17]. Therefore, the pretreatment of

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hardness must be applied before the advanced treatment of boron. The use of precipitation, one of the conventional methods, in the pretreatment of hardness causes the total treatment cost increase because of the high caustic consumption [14]. Consequently, an applicable and cost-effective method is needed for the pretreatment of these wastewaters.

Zeolites are aluminosilicate minerals that contain interchangeable alkali and alkaline earth metal cations in addition to water being in the structural framework. Clinoptilolite is one of the most abundant natural zeolite species in the world and founds in relatively large pelitic sedimentary deposits in sufficiently high purity [18] and is a native mineral used to remove cations [19].

Generally, the main purpose of the optimization is to determine the level of independent variables resulting in a maximum (or minimum) response without spending too much time with too many experiments on a particular area of interest. These processes can be accomplished using the response surface methodology (RSM) approach, which includes central composite design (CCD), Doehlert matrix, and Box–Behnken design. Among them, CCD is a standard RSM design widely used to fit a second-order model [20]. RSM is an optimization method that is used frequently in industrial wastewater treatment [21–23].

In Bigadiç Etimaden Boron Plant, the wastewaters sourced from open pits and boron mineral washing processes are stored in wastewater dam and the stored wastewater contains the high concentration of boron and hardness. Because of the limited capacity of the wastewater dam, the plant set up a pilot-scale membrane unit ended with RO to treat and reuse the wastewater, but the hardness forms scale on the membrane surface. Therefore, the determination of a feasible and cost-effective method for hardness removal from wastewater has great importance for sustainable membrane applications. On the other hand, the clinoptilolite is found as an accompanying mineral of boron mineral in boron deposits of the plant. Therefore, the raw clinoptilolite is produced as a by-product in that plant. Hence, it was thought that the use of raw and modified clinoptilolite for the pretreatment of hardness from wastewater containing high boron could be feasible and cost-effective.

In this study, the determination of optimum conditions of the hardness removal from boron-containing wastewaters by using raw and modified clinoptilolite was aimed. Based on the results of the study, further studies such as preparation of clinoptilolite for column application, regeneration of consumed material and feasibility could be performed.

2. Material and methods

The wastewater used in experiments was supplied from the wastewater dam in the Bigadiç Etimaden Boron Plant. The characterization of wastewater is given in Table 1. To remove total and calcium hardness, the clinoptilolite mineral which is known as abundant and cheap material in nature was used. In the study, the raw, NaOH-modified and HCl-modified clinoptilolite minerals were used. In the preparation of the modified samples, the clinoptilolite was firstly dried, and then weighed on a precision scale and treated with 1 M of HCl or NaOH solution for 24 h. Finally, the suspensions were filtered and dried.

Table 1
Characterization of wastewater

pH	8.66
Conductivity (µS/cm)	2,137
Total hardness (mg $CaCO_3$/L)	658.784
Calcium hardness (mg $CaCO_3$/L)	211.68
Boron (mg/L)	602.89

The RSM, a collection of mathematical and statistical techniques, is useful for analyzing the effects of several independent variables on the response [24]. Therefore, the experiments were carried out under conditions determined by the CCD of RSM. The clinoptilolite dosage, contact time, temperature and dilution ratio were chosen as independent variables of RSM and total and calcium hardness removal capacity (mg/g) and efficiency (%) of clinoptilolite were chosen as dependent variables of RSM. The factors and levels of design are given in Table 2.

The experiments were carried out in polyethylene bottles and 100 mL of wastewater was used for each experiment. The total and calcium hardness values were measured using the Standard Methods of 5340-C EDTA and 3500-Ca B codes [25]. The removal efficiency (%) and removal capacity (q) are calculated according to Eqs. (1) and (2).

$$\%\text{Removal efficiency} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

$$q(\text{mg/g}) = \frac{(C_0 - C) \times V}{W} \quad (2)$$

where C_0 and C are the hardness concentration of wastewater in (mg/L), V is the volume of wastewater in (L) and W is the mass of the clinoptilolite sample in (g).

3. Results

In this research, CCD of RSM was applied to evaluate the total and the calcium hardness removal efficiency and capacity from wastewater. The complete quadratic design model was composed of 25 experimental runs with 6 replicates at the central point. The run numbers and the variables (coded) are given in columns 1 and 2 of Table 3. The removal efficiencies for the raw and modified samples were also given in other columns of Table 3.

Table 2
Factors and levels of design

No.	Factors code	Response surfaces and levels				
		−α	−1	0	1	+α
1	X_1 = Dosage (g/L)	20	40	60	80	100
2	X_2 = Contact time(min)	30	60	90	120	150
3	X_3 = Temperature(°C)	15	20	25	30	35
4	X_4 = Dilution ratio	0.2	0.4	0.6	0.8	1

Table 3
Central composite design (CCD) for the study of four experimental variables and experimental results in the removal of total and calcium hardness

Run number	Variables (coded)				Raw clinoptilolite (removal, %)		HCl-modified clinoptilolite (removal, %)		NaOH-modified clinoptilolite (removal, %)	
	X_1	X_2	X_3	X_4	Total hardness	Calcium hardness	Total hardness	Calcium hardness	Total hardness	Calcium hardness
1	40	60	20	0.4	10.78	14.91	9.07	14.91	81.59	86.00
2	80	60	20	0.4	10.55	10.56	9.82	10.56	91.57	93.00
3	40	120	20	0.4	13.26	11.73	11.20	11.73	85.88	87.75
4	80	120	20	0.4	9.81	1.48	0.15	1.48	92.97	94.50
5	40	60	30	0.4	9.82	10.56	11.20	10.56	83.84	87.75
6	80	60	30	0.4	6.15	5.08	0.10	5.08	94.38	96.50
7	40	120	30	0.4	3.96	3.25	3.00	3.25	87.70	91.50
8	80	120	30	0.4	2.15	0.10	0.18	0.10	95.90	96.60
9	40	60	20	0.8	9.81	15.63	26.76	15.63	58.64	68.92
10	80	60	20	0.8	10.55	13.83	0.20	13.83	78.60	87.56
11	40	120	20	0.8	10.18	14.30	27.52	14.30	67.90	76.91
12	80	120	20	0.8	7.59	11.56	6.80	11.56	85.73	88.46
13	40	60	30	0.8	7.04	15.15	23.04	15.15	70.02	79.59
14	80	60	30	0.8	6.86	9.39	2.47	9.39	88.01	91.97
15	40	120	30	0.8	7.96	13.83	23.04	13.83	67.90	80.44
16	80	120	30	0.8	1.07	6.18	3.91	6.18	88.62	91.12
17	20	90	25	0.6	9.63	14.46	30.17	14.46	68.61	62.21
18	100	90	25	0.6	5.79	3.63	4.27	3.63	98.54	95.46
19	60	30	25	0.6	12.06	12.70	11.04	12.70	70.04	88.54
20	60	150	25	0.6	4.77	5.39	16.11	5.39	79.07	83.60
21	60	90	15	0.6	8.67	12.70	0.32	12.70	70.96	84.76
22	60	90	35	0.6	2.95	2.49	4.27	2.49	95.24	97.04
23	60	90	25	0.2	9.98	6.53	0.04	6.53	97.86	94.71
24	60	90	25	1	14.24	19.73	28.90	19.73	85.73	92.29
25	60	90	25	0.6	12.71	14.08	6.60	14.08	86.74	92.69
26	60	90	25	0.6	14.99	15.47	4.77	15.47	86.54	93.07
27	60	90	25	0.6	14.08	16.60	4.77	16.60	86.64	92.95
28	60	90	25	0.6	12.71	14.21	4.57	14.21	86.84	92.82
29	60	90	25	0.6	13.17	16.60	6.60	16.60	86.84	92.95
30	60	90	25	0.6	13.17	16.60	4.57	16.60	86.44	92.95
31	60	90	25	0.6	13.63	14.21	5.32	14.21	86.84	92.95

The plots of the predicted values (RSM) versus the experimental values (EXP) in the removal of total and calcium hardness using raw and modified clinoptilolite are shown in Figs. 1, 2 and 3. According to Figs. 1–3, there is an effective compatibility between predicted and experimental results.

The experimental results of removal capacity obtained for the raw and modified clinoptilolite are also given in Table 4. The plots of RSM-predicted versus EXP values of total hardness and calcium hardness removal capacities in case of the use of raw, HCl-modified and NaOH-modified clinoptilolite are shown in Figs. 4–6. According to Figs. 4–6, there is effective compatibility between predicted (RSM) and EXP results.

The equations and regression values (R^2) for removal efficiency and removal capacity obtained by RSM analyses of the experimental results are shown in Tables 5 and 6. The high R^2 values which are above 0.9 in Tables 5 and 6 indicate the accuracy of models. The tables demonstrate that the second-order polynomial models were highly significant and fitted very well to the experimental data. Therefore, the quadratic models were significant for removal efficiency (%) and removal capacity (mg/g).

The analysis of variance (ANOVA) analysis shows which proportion the equation represents the concrete relevance between principal changeable parameter and response [26]. The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using ANOVA. The ANOVA analysis was performed for the design experiments of each material. As the best results were obtained for NaOH-modified clinoptilolite,

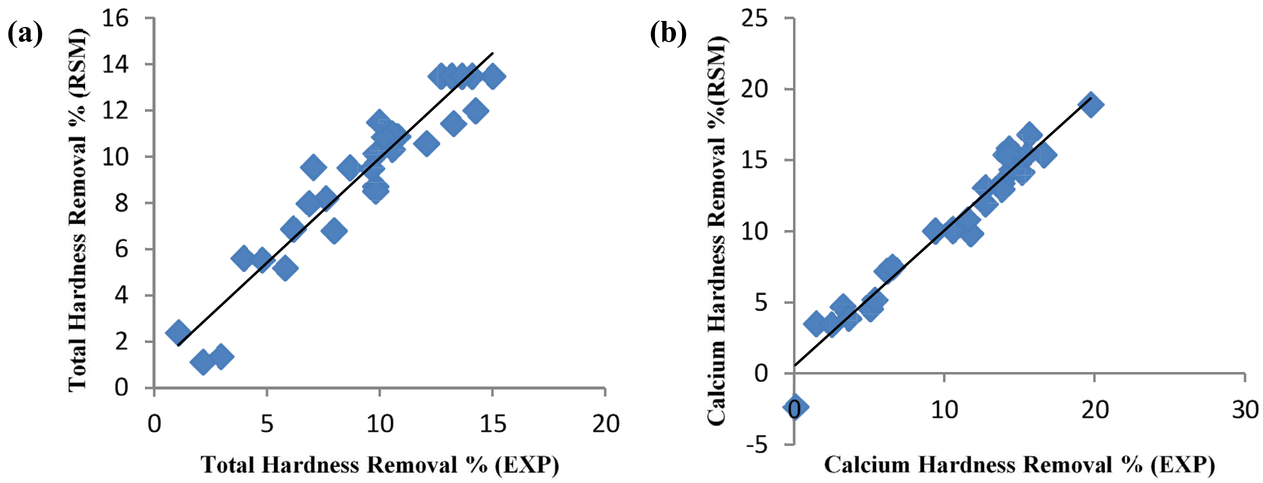

Fig. 1. Plots of RSM-predicted versus EXP values for raw clinoptilolite (a) total hardness removal and (b) calcium hardness removal.

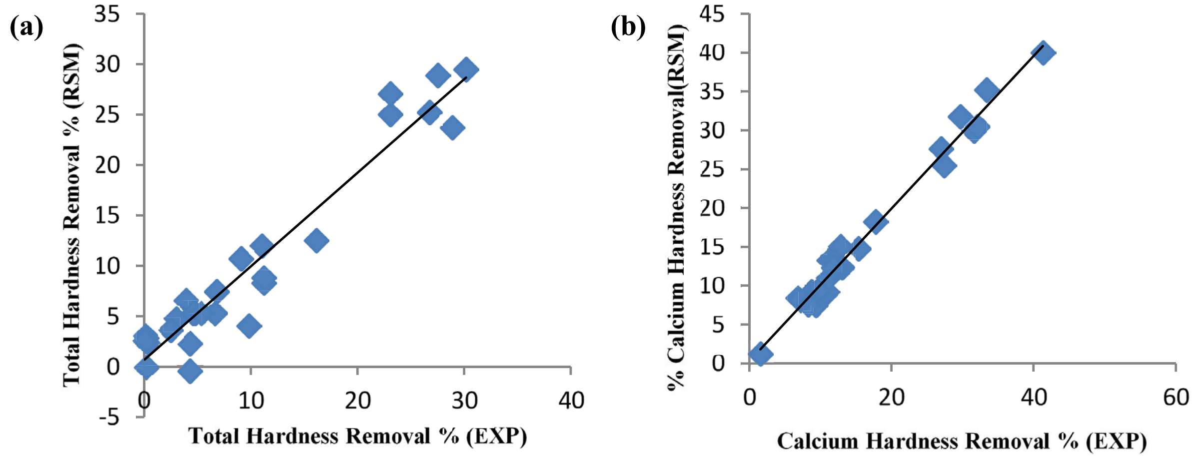

Fig. 2. Plots of RSM-predicted versus. EXP values for HCl-modified clinoptilolite (a) total hardness removal and (b) calcium hardness removal.

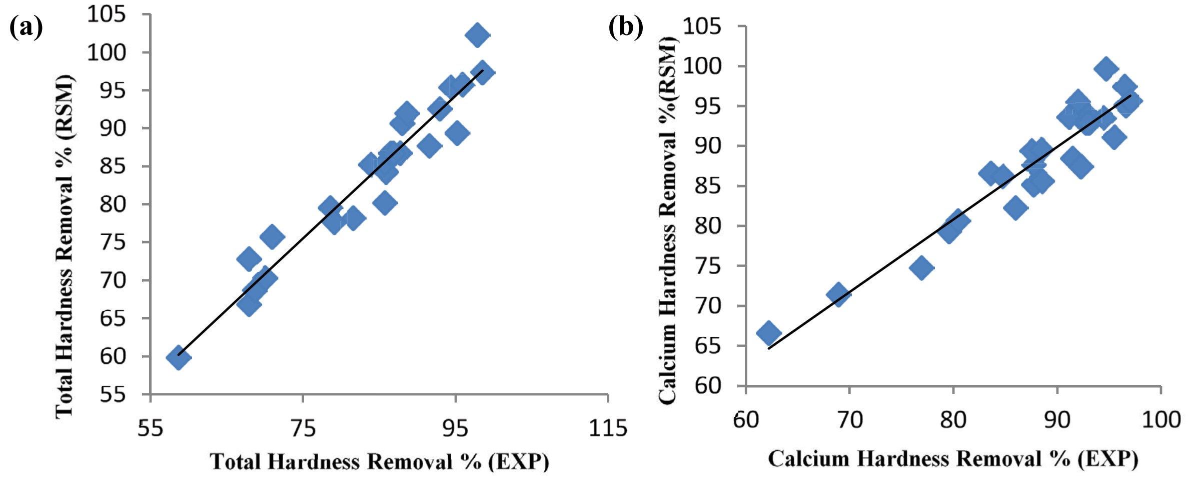

Fig. 3. Plots of RSM-predicted vs. EXP values for NaOH- modified clinoptilolite (a) total hardness removal and (b) calcium hardness removal.

Table 4
Central composite design (CCD) for the study of four experimental variables and experimental results in removal capacity

Run number	Variables (coded)				Raw clinoptilolite q (mg/g)		HCl-modified clinoptilolite q (mg/g)		NaOH-modified clinoptilolite q (mg/g)	
	X_1	X_2	X_3	X_4	Total hardness	Calcium hardness	Total hardness	Calcium hardness	Total hardness	Calcium hardness
1	40	60	20	0.4	0.75	0.32	0.71	0.32	5.37	1.82
2	80	60	20	0.4	0.35	0.11	0.35	0.11	3.02	0.98
3	40	120	20	0.4	0.87	0.25	0.87	0.25	5.66	1.86
4	80	120	20	0.4	0.32	0.02	0.32	0.02	3.06	1.00
5	40	60	30	0.4	0.65	0.22	0.65	0.22	5.52	1.86
6	80	60	30	0.4	0.20	0.05	0.20	0.05	3.11	1.02
7	40	120	30	0.4	0.26	0.07	0.26	0.07	5.78	1.94
8	80	120	30	0.4	0.07	0.00	0.07	0.00	3.16	1.02
9	40	60	20	0.8	1.29	0.66	1.29	0.66	7.73	2.92
10	80	60	20	0.8	0.70	0.29	0.70	0.29	5.18	1.85
11	40	120	20	0.8	1.34	0.61	1.34	0.61	8.95	3.26
12	80	120	20	0.8	0.50	0.24	0.50	0.24	5.65	1.87
13	40	60	30	0.8	0.93	0.64	0.93	0.64	9.23	3.37
14	80	60	30	0.8	0.45	0.20	0.45	0.20	5.80	1.95
15	40	120	30	0.8	1.05	0.59	1.05	0.59	8.95	3.41
16	80	120	30	0.8	0.07	0.13	0.07	0.13	5.84	1.93
17	20	90	25	0.6	1.90	0.92	1.90	0.92	13.56	3.95
18	100	90	25	0.6	0.23	0.05	0.23	0.05	3.05	1.21
19	60	30	25	0.6	0.79	0.27	0.79	0.27	4.61	1.87
20	60	150	25	0.6	0.31	0.11	0.31	0.11	5.21	1.77
21	60	90	15	0.6	0.57	0.27	0.57	0.27	4.67	1.79
22	60	90	35	0.6	0.19	0.05	0.19	0.05	6.27	2.05
23	60	90	25	0.2	0.20	0.05	0.20	0.05	2.05	0.67
24	60	90	25	1	1.56	0.70	1.56	0.70	9.41	3.26
25	60	90	25	0.6	0.84	0.30	0.84	0.30	10.05	1.96
26	60	90	25	0.6	0.99	0.33	0.99	0.33	10.09	1.97
27	60	90	25	0.6	0.93	0.35	0.93	0.35	10.10	1.97
28	60	90	25	0.6	0.84	0.30	0.84	0.30	10.11	1.96
29	60	90	25	0.6	0.87	0.35	0.87	0.35	10.11	1.97
30	60	90	25	0.6	0.87	0.35	0.87	0.35	10.09	1.97
31	60	90	25	0.6	0.90	0.30	0.90	0.30	10.11	1.97

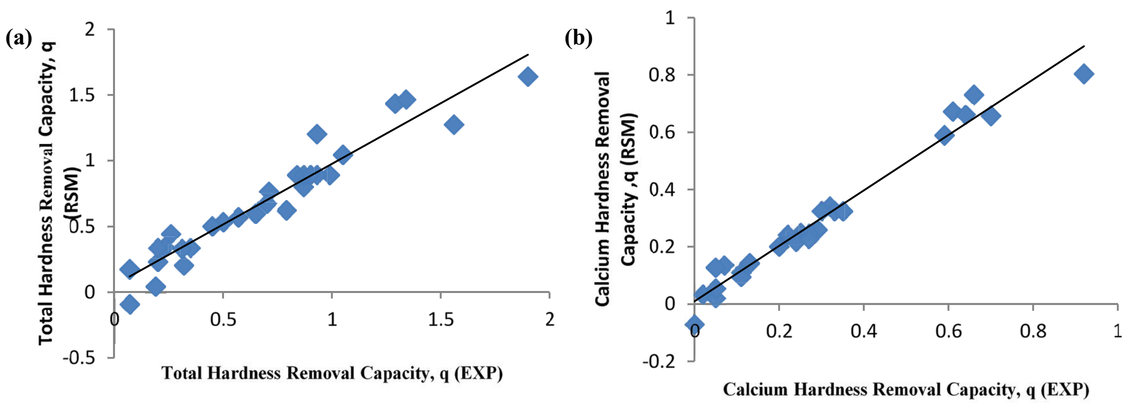

Fig. 4. Plots of RSM-predicted versus EXP values for raw clinoptilolite (a) total hardness removal capacity and (b) calcium hardness removal capacity.

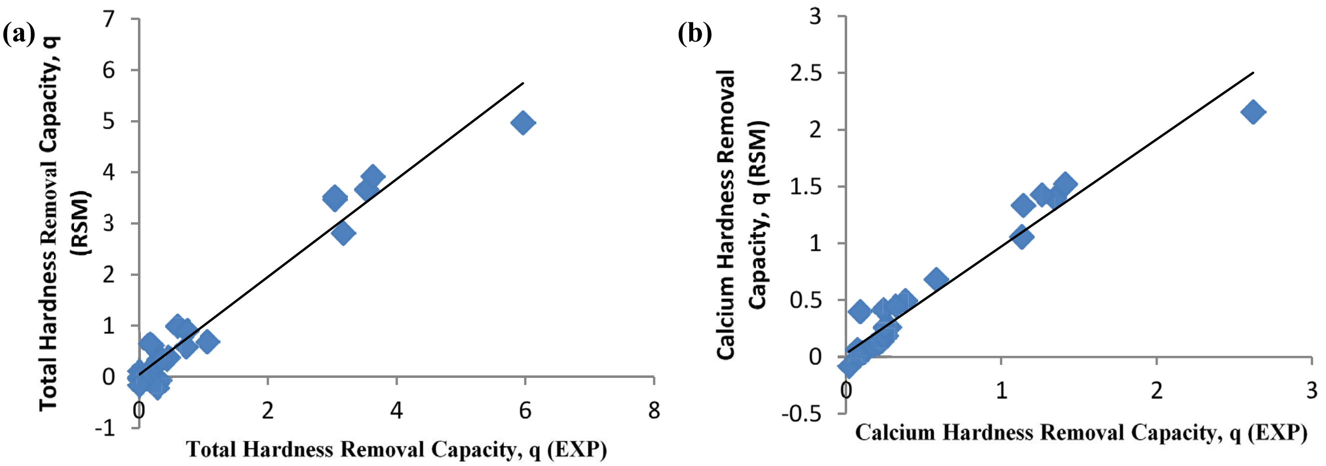

Fig. 5. Plots of RSM-predicted versus EXP values for HCl-modified clinoptilolite (a) total hardness removal capacity and (b) calcium hardness removal capacity.

the ANOVA results of the NaOH-modified clinoptilolite are given for removal and removal capacity in Tables 7 and 8. According to the ANOVA analysis, the parameters with $p \leq 0.05$ are effective in the process. The effective parameters on the process are signed as bold in the *p*-value column of tables.

The optimum conditions were determined in the above 95% confidence level. The confirmation experiments were carried out in the optimum conditions determined by RSM. The comparison of the model outputs with results of confirmation experiments is given in Table 9. It can be seen from Table 9 that the experimental results compatible with the model results.

The contour graph obtained by RSM shows the effect of two factors on removal efficiency and removal capacity. The contour graphs of the experiments carried out with NaOH-modified clinoptilolite are demonstrated in Figs. 7 and 8.

Table 5
RSM-based models and R^2 values for removal efficiency

Responses			Final equation in terms of factors	R^2
Raw clinoptilolite	Total hardness	% Removal efficiency	% Total hardness removal = –68.8 + 0.621X_1 + 0.442X_2 + 4.131X_3 + 1.8X_4 – 0.003 840X_1 × X_1 – 0.001511X_2 × X_2 – 0.0804X_3 × X_3 – 10.90X_4 × X_4 – 0.001187X_1 × X_2 – 0.00439X_1 × X_3 + 0.0038X_1 × X_4 – 0.00578X_2 × X_3 + 0.0069X_2 × X_4 + 0.445X_3 × X_4	0.9065
	Calcium hardness	% Removal efficiency	% Calcium hardness removal = –36.7 + 0.394X_1 + 0.194X_2 + 3.239X_3 – 3.7X_4 – 0 .003910X_1 × X_1 – 0.001738X_2 × X_2 – 0.0771X_3 × X_3 – 13.57X_4 × X_4 – 0.000667X_1 × X_2 – 0.00181X_1 × X_3 + 0.0825X_1 × X_4 – 0.00040X_2 × X_3 + 0.1710X_2 × X_4 + 0.557X_3 × X_4	0.9561
HCl–modified clinoptilolite	Total hardness	% Removal efficiency	%Hardness removal = 27.5 – 0.642X_1 – 0.451X_2 + 1.87X_3 – 7.3X_4 + 0.00661X_1 × X_1 + 0.001927X_2 × X_2 – 0.0434X_3 × X_3 + 48.9X_4 × X_4 + 0.00039X_1 × X_2 + 0.00248X_1 × X_3 – 0.981X_1 × X_4 – 0.00271X_2 × X_3 + 0.255X_2 × X_4 + 0.434X_3 × X_4	0.9287
	Calcium hardness	% Removal efficiency	%Calcium hardness removal = 9.9 – 0.592X_1 + 0.048X_2 + 3.039X_3 – 45.2X_4 + 0.0 07337X_1 × X_1 – 0.000642X_2 × X_2 – 0.0201X_3 × X_3 + 59.40X_4 × X_4 + 0.001448X_1 × X_2 – 0.01919X_1 × X_3 – 0.563X_1 × X_4 – 0.00964X_2 × X_3 + 0.3019X_2 × X_4 + 0.089X_3 × X_4	0.9830
NaOH-modified clinoptilolite	Total hardness	% Removal efficiency	%Total hardness removal = 27.6 + 0.254X_1 + 0.890X_2 + 2.82X_3 – 125.2X_4 – 0.00229X_1 × X_1 – 0.003522X_2 × X_2 – 0.0413X_3 × X_3 + 28.5X_4 × X_4 – 0.00048X_1 × X_2 + 0.00162X_1 × X_3 + 0.636X_1 × X_4 – 0.00759X_2 × X_3 + 0.040X_2 × X_4 + 0.867X_3 × X_4	0.9374
	Calcium hardness	% Removal efficiency	%Calcium hardness removal = 16.9 + 1.347X_1 + 0.502X_2 + 1.65X_3 – 61.8X_4 – 0.00876X_1 × X_1 – 0.001885X_2 × X_2 – 0.0196X_3 × X_3 + 4.0X_4 × X_4 – 0.00132X_1 × X_2 – 0.00439X_1 × X_3 + 0.401X_1 × X_4 – 0.00345X_2 × X_3 + 0.019X_2 × X_4 + 0.636X_3 × X_4	0.9079

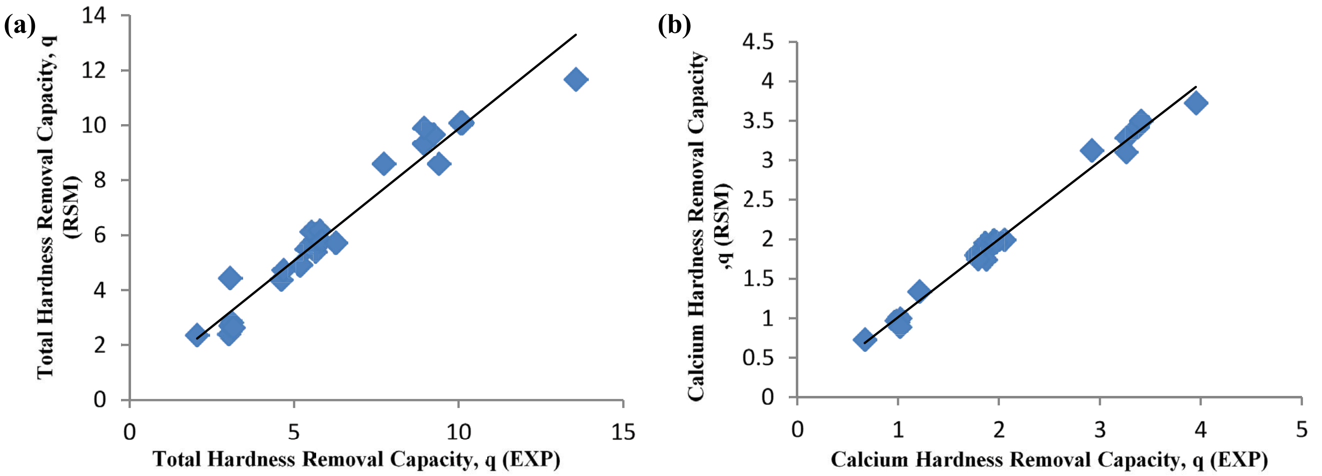

Fig. 6. Plots of RSM-predicted versus EXP values for NaOH-modified clinoptilolite (a) total hardness removal capacity and (b) calcium hardness removal capacity.

Table 6
RSM-based models and R^2 values for removal capacity

Responses			Final equation in terms of factors	R^2
Raw clinoptilolite	Total hardness	q	q (mg/g) = –4.38 – 0.0086X_1(g/L) + 0.0305X_2(min) + 0.2949X_3(°C) + 3.48X_4 + 0.000063X_1(g/L) × X_1(g/L) – 0.000115X_2(min) × X_2(min) – 0.00584X_3(°C) × X_3(°C) – 0.525X_4 × X_4 – 0.000071X_1(g/L) × X_2(min) + 0.000150X_1(g/L) × X_3(°C) – 0.0209X_1(g/L) × X_4 – 0.000317X_2(min) × X_3(°C) – 0.00021X_2(min) × X_4 – 0.0162X_3(°C) × X_4	0.9223
	Calcium hardness	q	q (mg/g) = –0.734 – 0.01122X_1(g/L) + 0.00583X_2(min) + 0.0796X_3(°C) + 1.103X_4 + 0.000088X_1(g/L) × X_1(g/L) – 0.000043X_2(min) × X_2(min) – 0.001840X_3(°C) × X_3(°C) + 0.193X_4 × X_4 + 0.000006X_1(g/L) × X_2(min) + 0.000025X_1(g/L) × X_3(°C) – 0.01500X_1(g/L) × X_4 – 0.000025X_2(min) × X_3(°C) + 0.00146X_2(min) × X_4 + 0.0075X_3(°C) × X_4	0.9684
HCl-modified clinoptilolite	Total hardness	q	q (mg/g) = 2.31 – 0.1639X_1(g/L) – 0.0175X_2(min) + 0.216X_3(°C) + 5.46X_4 + 0.001541X_1(g/L) × X_1(g/L) + 0.000082X_2(min) × X_2(min) – 0.00449X_3(°C) × X_3(°C) + 6.16X_4 × X_4 + 0.000055X_1(g/L) × X_2(min) + 0.00071X_1(g/L) × X_3(°C) – 0.1627X_1(g/L) × X_4 – 0.000329X_2(min) × X_3(°C) + 0.0141X_2(min) × X_4 – 0.026X_3(°C) × X_4	0.9555
	Calcium hardness	q	q (mg/g) = 0.38 – 0.0636X_1(g/L) + 0.0059X_2(min) + 0.1045X_3(°C) + 1.60X_4 + 0.000637X_1(g/L) × X_1(g/L) – 0.000032X_2(min) × X_2(min) – 0.00110X_3(°C) × X_3(°C) + 1.686X_4 × X_4 + 0.000036X_1(g/L) × X_2(min) – 0.000381X_1(g/L) × X_3(°C) – 0.0477X_1(g/L) × X_4 – 0.000263X_2(min) × X_3(°C) + 0.00594X_2(min) × X_4 + 0.0006X_3(°C) × X_4	0.9442
NaOH-modified clinopilolite	Total hardness	q	q (mg/g) = –50.50 + 0.1044X_1(g/L) + 0.2964X_2(min) + 2.512X_3(°C) + 40.89X_4 – 0.001265X_1(g/L) × X_1(g/L) – 0.001505X_2(min) × X_2(min) – 0.04860X_3(°C) × X_3(°C) – 28.75X_4 × X_4 – 0.000093X_1(g/L) × X_2(min) – 0.00048X_1(g/L) × X_3(°C) – 0.0377X_1(g/L) × X_4 – 0.00081X_2(min) × X_3(°C) + 0.0084X_2(min) × X_4 + 0.116X_3(°C) × X_4	0.9602
	Calcium hardness	q	q (mg/g) = 0.37 – 0.0423X_1(g/L) + 0.01488X_2(min) + 0.0672X_3(°C) + 3.97X_4 + 0.000355X_1(g/L) × X_1(g/L) – 0.000053X_2(min) × X_2(min) – 0.000921X_3(°C) × X_3(°C) – 0.295X_4 × X_4 – 0.000050X_1(g/L) × X_2(min) – 0.000312X_1(g/L) × X_3(°C) – 0.02969X_1(g/L) × X_4 – 0.000133X_2(min) × X_3(°C) + 0.00250X_2(min) × X_4 + 0.0363X_3(°C) × X_4	0.9889

Table 7
Analysis of variance (ANOVA) for removal efficiency NaOH-modified clinoptilolite (a) total hardness and (b) calcium hardness

Source	DF	Adj. SS	Adj. MS	*F*-Value	*P*-Value
(a)					
Model	14	2,851.78	203.70	17.11	0.000
X_1	1	1,235.10	1,235.10	103.76	0.000
X_2	1	80.70	80.70	6.78	0.000
X_3	1	280.51	280.51	23.56	0.000
X_4	1	733.39	733.39	61.61	0.000
X_1^2	1	23.91	23.91	2.01	0.176
X_2^2	1	287.25	287.25	24.13	0.000
X_3^2	1	30.52	30.52	2.56	0.129
X_4^2	1	37.20	37.20	3.13	0.096
X_1X_2	1	1.34	1.34	0.11	0.742
X_1X_3	1	0.42	0.42	0.04	0.853
X_1X_4	1	103.48	103.48	8.69	0.009
X_2X_3	1	20.73	20.73	1.74	0.206
X_2X_4	1	0.91	0.91	0.08	0.786
X_3X_4	1	12.02	12.02	1.01	0.330
Lack-of-Fit	10	190.30	19.03	726.60	0.000
(b)					
Model	14	1,746.21	124.729	11.27	0.000
X_1	1	904.67	904.67	81.72	0.000
X_2	1	1.56	1.556	0.14	0.713
X_3	1	135.04	135.04	12.20	0.003
X_4	1	224.91	224.91	20.32	0.000
X_1^2	1	351.31	351.31	31.73	0.000
X_2^2	1	82.28	82.282	7.43	0.015
X_3^2	1	6.83	6.832	0.62	0.444
X_4^2	1	0.74	0.743	0.07	0.799
X_1X_2	1	10.06	10.065	0.91	0.355
X_1X_3	1	3.09	3.089	0.28	0.605
X_1X_4	1	41.12	41.120	3.71	0.072
X_2X_3	1	4.30	4.295	0.39	0.542
X_2X_4	1	0.20	0.200	0.02	0.895
X_3X_4	1	6.46	6.464	0.58	0.456
Lack-of-Fit	10	177.03	17.703	1,200.42	0.000

Table 8
Analysis of variance (ANOVA) for removal capacity (*q*) NaOH-modified clinoptilolite (a) total hardness and (b) calcium hardness

Source	DF	Adj. SS	Adj. MS	*F*-Value	*P*-Value
(a)					
Model	14	249.918	17.8513	27.57	0.000
X_1	1	78.446	78.4455	121.15	0.000
X_2	1	0.451	0.4510	0.70	0.416
X_3	1	1.485	1.4850	2.29	0.149
X_4	1	58.188	58.1882	89.87	0.000
X_1^2	1	7.327	7.3266	11.32	0.004
X_2^2	1	52.497	52.4967	81.08	0.000
X_3^2	1	42.209	42.2086	65.19	0.000
X_4^2	1	37.813	37.8130	58.40	0.000
X_1X_2	1	0.050	0.0495	0.08	0.786
X_1X_3	1	0.037	0.0371	0.06	0.814
X_1X_4	1	0.363	0.3630	0.56	0.465
X_2X_3	1	0.238	0.2377	0.37	0.553
X_2X_4	1	0.041	0.0410	0.06	0.805
X_3X_4	1	0.214	0.2139	0.33	0.573
Lack-of-Fit	10	10.357	1.0357	2242.30	0.000
(b)					
Model	14	18.0804	1.29146	101.38	0.000
X_1	1	0.0043	0.00427	0.33	0.571
X_2	1	0.0043	0.00427	0.33	0.571
X_3	1	0.0888	0.08882	6.97	0.018
X_4	1	8.4491	8.44907	663.24	0.000
X_1^2	1	0.5763	0.57631	45.24	0.000
X_2^2	1	0.0660	0.06598	5.18	0.037
X_3^2	1	0.0152	0.01517	1.19	0.291
X_4^2	1	0.0040	0.00397	0.31	0.584
X_1X_2	1	0.0144	0.01440	1.13	0.303
X_1X_3	1	0.0156	0.01563	1.23	0.284
X_1X_4	1	0.2256	0.22562	17.71	0.001
X_2X_3	1	0.0064	0.00640	0.50	0.489
X_2X_4	1	0.0036	0.00360	0.28	0.602
X_3X_4	1	0.0210	0.02103	1.65	0.217
Lack-of-Fit	10	0.2037	0.02037	855.47	0.000

Table 9
Optimum conditions and the comparison of the model outputs with confirmation experiments at optimum conditions

	Optimum conditions				Comparison of model and experimental results							
					Total hardness removal efficiency (%)		Total hardness removal capacity (q)		Calcium hardness removal efficiency (%)		Calcium hardness removal capacity (q)	
Material type	Dosage (g/L)	Contact time (min)	Temperature (°C)	Dilution ratio	Model outputs	Experimental values	Model outputs	Experimental values	Model outputs	Experimental values	Model outputs	Experimental values
Raw Clinoptilolite	55	82	23	0.6	14.22	13.92	–	–	–	–	–	–
	20	97	21	1	–	–	2.43	2.00	–	–	–	–
	47	93	24	1	–	–	–	–	19.67	19.45	–	–
	20	80	23	1	–	–	–	–	–	–	1.39	1.36
HCl–modified clinoptilolite	20	150	23	1	76.23	69.17	–	–	–	–	–	–
	20	150	17	1	–	–	10.86	10.8	–	–	–	–
	20	32	35	1	–	–	–	–	76.06	68.81	–	–
	20	52	35	1	–	–	–	–	–	–	3.84	3.68
NaOH–modified clinoptilolite	84	89	29	0.2	100	99.10	–	–	–	–	–	–
	20	93	26	0.8	–	–	12.61	12.30	–	–	–	–
	68	82	31	0.2	–	–	–	–	100	99.15	–	–
	20	110	35	1	–	–	–	–	–	–	5.66	5.92

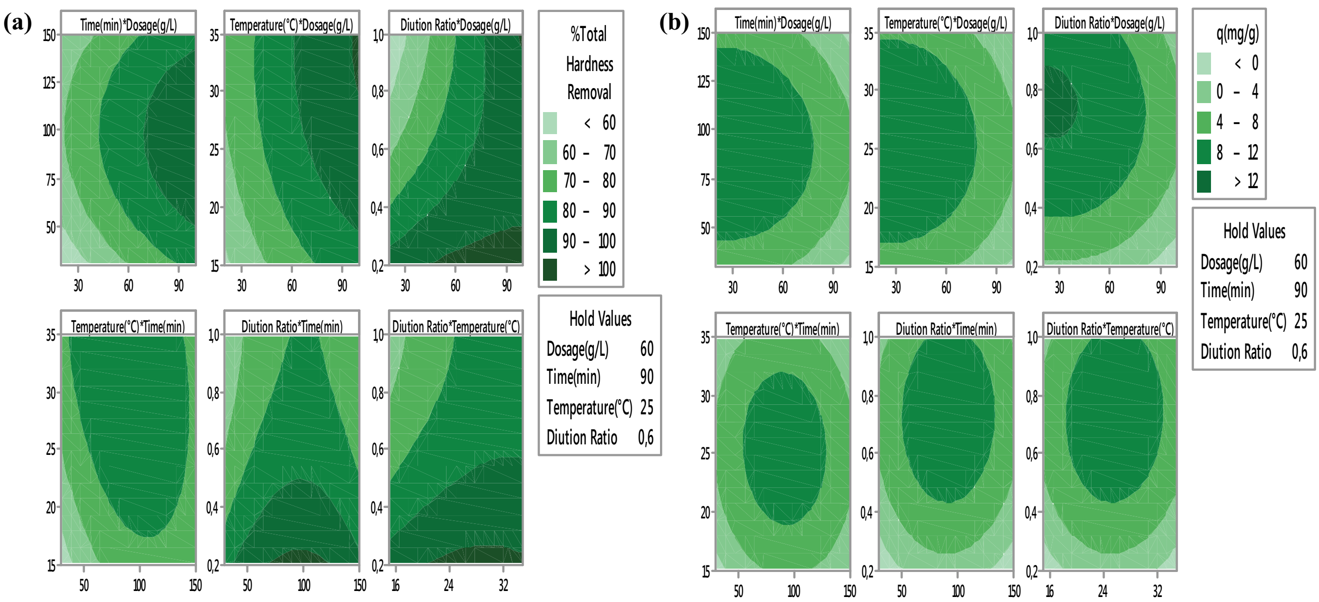

Fig. 7. Contour plots of NaOH-modified clinoptilolite (a) total hardness removal effect (%) and (b) total hardness removal capacity (q).

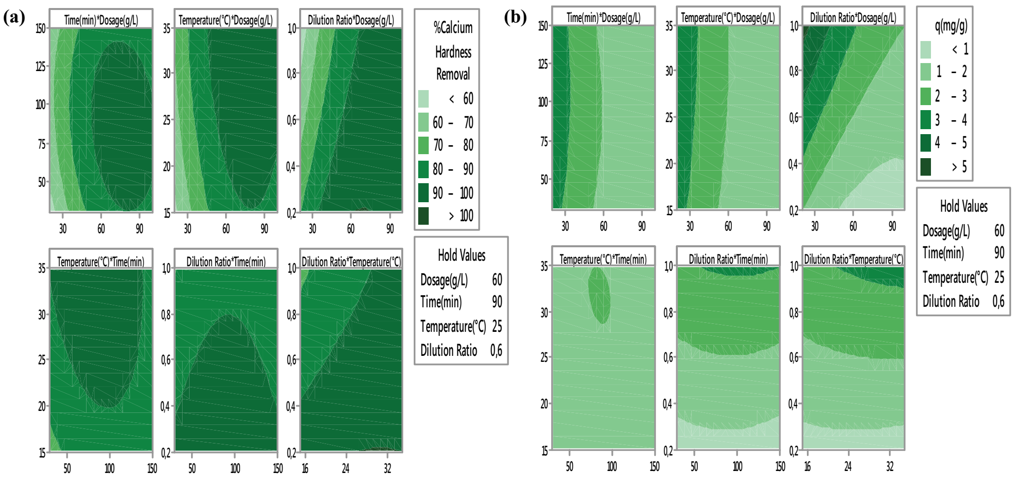

Fig. 8. Contour plots of NaOH-modified clinoptilolite(a) calcium hardness removal effect (%) and (b) calcium hardness removal capacity (*q*).

4. Conclusion

In this study, the raw and modified clinoptilolite minerals were used to remove the total and calcium hardness from the wastewater containing boron of high concentration. The effective parameters and the optimum conditions of removal efficiency and capacity were determined by RSM analysis, hereby empirical models were derived. As a result, NaOH-modified clinoptilolite which gives above 99% removal efficiency for total hardness and calcium hardness is selected as the most convenient material. The total and calcium hardness removal capacities of NaOH-modified clinoptilolite in the optimum conditions were obtained 12.30 and 5.92 mg/g, respectively.

Symbols

RSM	—	Response surface methodology
CCD	—	Central composite design
C	—	Hardness concentration of wastewater
C_0	—	Initial hardness concentration of wastewater
q	—	Removal capacity
W	—	Mass of the clinoptilolite sample
V	—	Volume of wastewater

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